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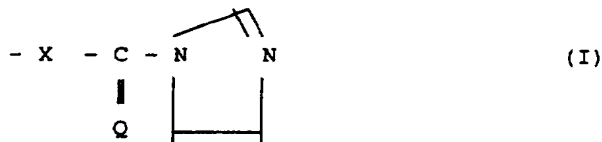
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Macromolecules Vol. 30 (7) pp.1890-1896 (1997)
Macromolecules Vol. 25 (21) pp.5561-5573 (1992)

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(54) Abstract Title
Hyperbranched polymers

(57) Hyperbranched polymers containing linkages selected from urea, urethane, carbonate, ester and amine linkages are described. A hyperbranched polymer is prepared by reacting a polyfunctional compound having three reactive functional groups (B) in substantially equimolar quantities with a reagent which reacts rapidly with group (B) to form a group (A) which reacts more slowly with group (B), or by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), either (A) or (B) being a group of the formula:



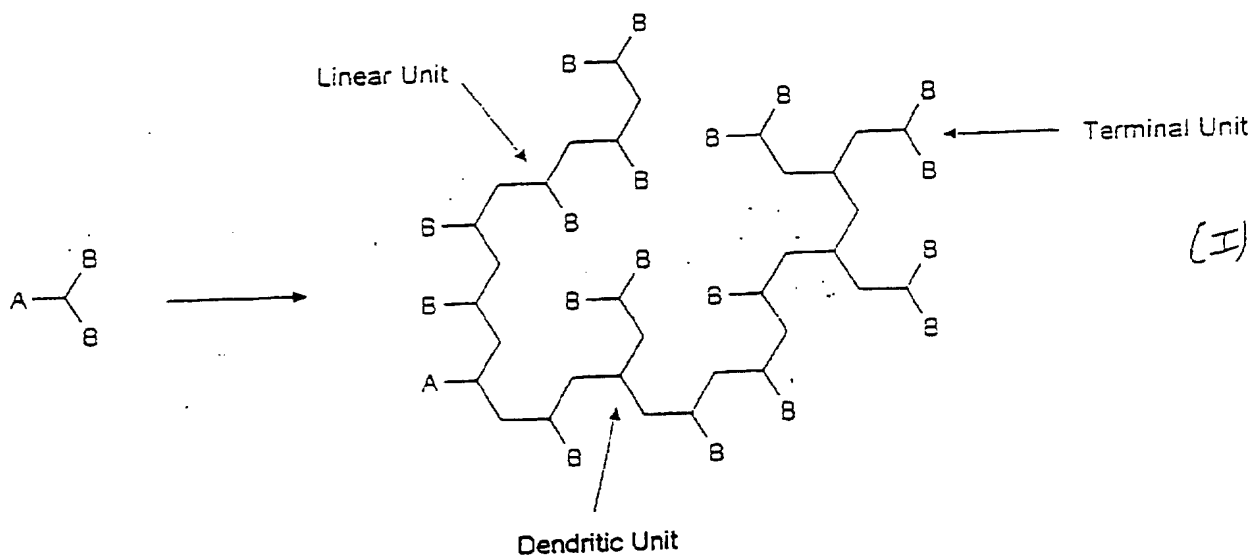
where Q represents O or S and X represents -O-, -S-, -NH- or a direct bond.

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Polymers and their Preparation

This invention relates to highly branched polymers known as hyperbranched polymers and to reactions for their preparation.

Hyperbranched polymers are generally prepared by the polymerisation in a single reaction of a compound (monomer) containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A). Such a monomer will react as shown in Figure I below to form a branched polymer containing one group (A) and $(x+1)$ groups (B) if x monomer molecules have reacted together.



The polymerisation of an AB_2 monomer leads to a complex mixture of products containing both linear and dendritic regions. 3 subunits are found within a hyperbranched polymer formed from an AB_2 monomer. These differ in the number of B

functionalities which have reacted. If both have reacted a dendritic unit is formed, if only one has reacted a linear unit is formed and if no B groups have reacted a terminal unit is formed.

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The ratio of these units can be used to determine the degree of branching of the polymer.

$$\text{Degree of Branching} = \frac{\text{Number of Dendritic Units} + \text{Number of Terminal Units}}{\text{Total number of Units}}$$

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The degree of branching for an ideal dendrimer is equal to 1. A linear polymer has a degree of branching of 0. A hyperbranched polymer has a structure intermediate between a dendrimer and linear polymer and can in theory have a degree of branching between 0 and 1 but generally is only considered as a hyperbranched polymer when the degree of branching is greater than 0.4, as described in US-A-5514764.

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Hyperbranched polyesters are described for example in US-A-5418301, US-A-5514764 and WO-A-96/12754. Hyperbranched polycarbonates are described by D.H. Bolton and K. L. Wooley in *Macromolecules* 1997, vol. 30, page 1890. Hyperbranched polyphenylenes are described by Y.H. Kim and O.W. Webster in *Macromolecules* 1992, 25, 5562. Hyperbranched polyethers are described by K. E. Uhrich, C.J. Hawker, J.M.J. Frechet and S.R. Turner in *Macromolecules*, 1992, 25, 4583. Hyperbranched polyetherketones are described by F. Chu and C.J. Hawker in *Polymer Bulletin*, 1993, 30, 265. Hyperbranched polyurethanes are described by A. Kumar and S. Ramakrishnan in *J. Chem. Soc. Commun.* 1993, 18, 1453 and by R. Spindler and J.M.J. Frechet in *Macromolecules*, 1993, 26, 4809. Hyperbranched

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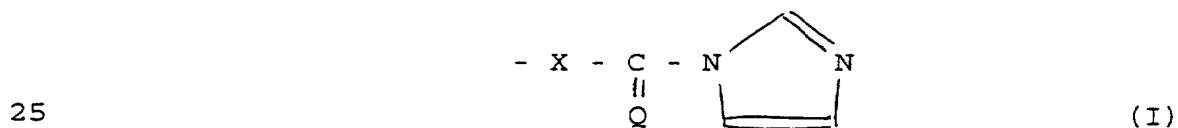
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poly(ester-amide)s are described by H.R. Kricheldorf and G. Lohden in Macromol. Chem. Phys, 1995, 196, 1839.

Hyperbranched polymers have wide industrial potential
5 for use in high solids coatings and sealants, as reactive
plasticisers and as substrates for binding biological
reagents such as enzymes or antigens owing to their
characteristics such as lower viscosity when molten or in
10 solution when compared to linear analogues, higher solubility
than their linear analogues and high chemical reactivity
(large number of reactive chain ends). There is a need for
further reactions capable of producing hyperbranched polymers
without premature crosslinking and without needing protection
and deprotection of reactive groups.

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A process according to one aspect of the present
invention for the preparation of a hyperbranched polymer by
the polymerisation of a compound containing a single group
(A) of one chemical type and at least two groups (B) of a
20 different chemical type which is reactive with (A) is
characterised in that the single group (A) is a group of the
formula:



where Q represents O or S and X represents -O-, -S-, -NH- or
a direct bond, the group being linked to the remainder of the
compound or polymer through a carbon atom.

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According to another aspect of the invention, a process
for the preparation of a hyperbranched polymer by the

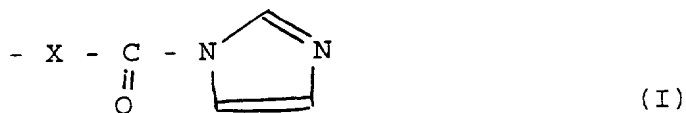
polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that either the group (A) or the group (B) is a group of the
5 formula:-



10 where Q represents O or S and X' represents -NH- or a direct bond, the group being linked to the remainder of the compound through a carbon atom.

The imidazolidine group of the formula:

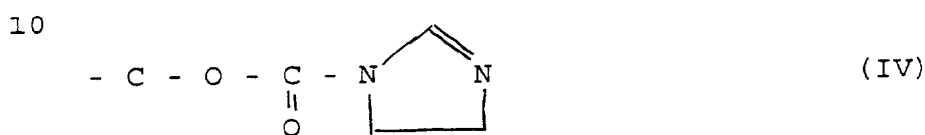
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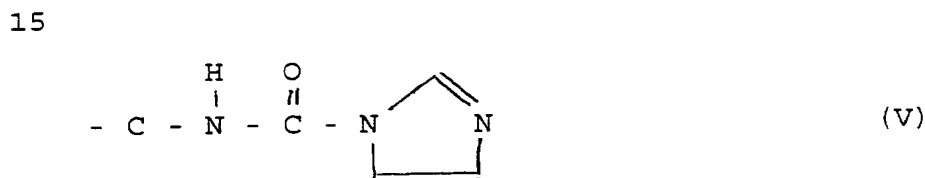
can in general be produced by reaction of a compound or
20 polymer containing hydroxyl, thiol, amine or carboxylic acid groups with carbonyl diimidazole or thiocarbonyl diimidazole. The imidazole ring can be substituted or can be fused to a benzene ring, leading to a substituted imidazole ring in the group of formula (I), but this is not preferred. The
25 preferred reagent is carbonyl diimidazole. Alcohol groups, thiol groups, primary amino groups and carboxylic acid groups react with carbonyl diimidazole to form an imidazolidine in which an active hydrogen atom of the alcohol, thiol and/or amino groups, and/or the whole carboxylic acid group is
30 replaced by a carbonyl imidazole group of the formula:



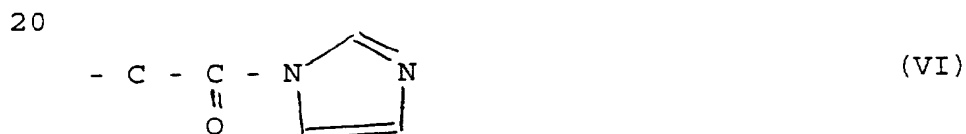
5 The term "imidazolidine" is used in this specification to describe a 1-imidazole carboxyl ester of an alcohol having the structure:



or a 1-imidazole carboxamide having the structure:



as well as an imidazolidine having the structure:



25 The imidazolidine group can be prepared in alternative ways, although preparation from carbonyl diimidazole is most convenient. 1-Imidazole carboxyl esters can be prepared by reaction of a chloroformate with imidazole or by reaction of the carbonyl chloride of imidazole with an alcohol. 1-Imidazole carboxamides can be prepared by reaction of a carbamoyl chloride with imidazole or by reaction of the carbonyl chloride of the imidazole with an amine. 1-Imidazole

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carbonyl compounds can be prepared by reaction of an acyl chloride with imidazole.

The imidazolidine group can in general be the single A
5 group in an AB_2 monomer, forming on polymerisation a hyperbranched polymer having terminal groups B which are the functional groups reactive with the imidazolidine, or the groups B in an AB_2 monomer can be imidazolidine groups, forming a hyperbranched polymer having terminal imidazolidine groups.
10 These terminal imidazolidine groups can be reacted in a further step to convert them to different groups if desired.

The group reacted with carbonyl diimidazole to form the group (A) or (B) of an AB_2 monomer is preferably a carboxylic
15 acid group or primary amine group. Carboxylic acid groups react with carbonyl diimidazole to replace one imidazole ring to form an imidazolidine readily at ambient temperature without need for a catalyst with little tendency towards further reaction to replace the remaining imidazole ring. Primary
20 amines are capable of reacting with carbonyl diimidazole at room temperature without need for a catalyst to replace both imidazole rings, forming a urea linkage, if the primary amine is present in stoichiometric excess, but if the reagents are used in stoichiometrically equivalent amounts or if the
25 carbonyl diimidazole is used in excess, the predominant reaction is to replace only one of the imidazole rings of the carbonyl diimidazole.

According to another aspect of the invention, a process
30 for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different

chemical type which is reactive with (A) is characterised in that a precursor compound, containing either a single group (A') of one chemical type reactive with carbonyl diimidazole and at least two groups (B) of a different chemical type from A' which is less reactive than A' with carbonyl diimidazole or at least two groups (B') of one chemical type reactive with carbonyl diimidazole and a single group (A) of a different chemical type from B' which is less reactive than B' with carbonyl diimidazole, is reacted with carbonyl diimidazole under conditions such that only the group A' or the groups B' react with the carbonyl diimidazole to form imidazolide groups, and the resulting compound containing imidazolide groups is polymerised under more vigorous reaction conditions to form the hyperbranched polymer.

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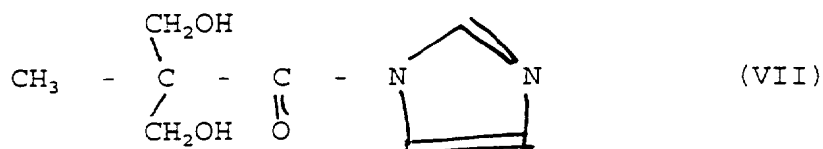
Alcohol groups will react readily with carbonyl diimidazole in the presence of a basic catalyst but only very slowly at room temperature without catalyst. Primary alcohol groups can react to replace both imidazole rings, forming a carbonate linkage, and are preferably not used in stoichiometric excess. Secondary and tertiary alcohol groups generally show little tendency to further reaction to replace the remaining imidazole ring.

25

This requirement for a catalyst or for heating can be used in a convenient method for preparing an AB₂ monomer and then polymerising it to form a hyperbranched polymer according to the invention. For example a precursor compound containing one carboxylic acid group (A') and two hydroxyl groups such as 2,2-bis(hydroxymethyl)propionic acid or 3,5-dihydroxybenzoic acid or the N,N-bis(2-hydroxyethyl) monoamide of adipic acid can be reacted with carbonyl

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diimidazole at room temperature without catalyst to form an imidazolide such as



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The hydroxyl group can for example be a primary alcohol group or an unhindered secondary alcohol group such as a -CHOHCH₃ group or a phenol group when the carboxylic acid is aliphatic; almost all primary and secondary alcohol and phenol groups are suitable if the carboxylic acid is aromatic. This compound containing one imidazolide group and two alcohol groups can be used as an AB₂ monomer. It is substantially stable at ambient temperature (up to 30°C) in the absence of catalyst. Under more vigorous conditions, for example when heated to at least 50°C, preferably 50-120°C, intermolecular reaction takes place between an alcohol group and an imidazolide group, forming a larger molecule containing one imidazolide group together with an ester linkage and alcohol groups and eventually a hyperbranched polyester having terminal hydroxyl groups. Alternatively the imidazolide can be polymerised by addition of a basic catalyst, for example KOH, NaOH, a quaternary ammonium hydroxide or a strongly basic amine such as diazabicycloundecene.

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Similarly a precursor compound containing one primary amine group (A') and two primary or secondary alcohol groups such as N-(3-aminopropyl) diethanolamine can be reacted with a substantially equimolar amount of carbonyl diimidazole to form an imidazolide such as

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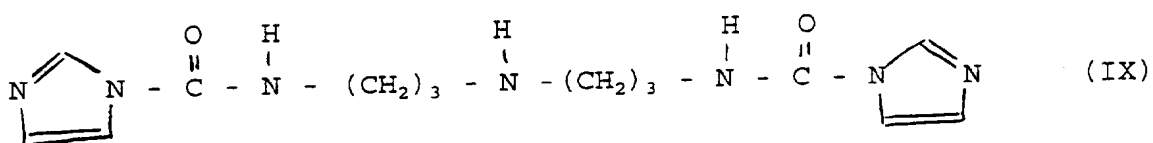
This is stable at ambient temperature in the absence of catalyst and can be used as an AB₂ monomer which is activated by heating or by basic catalyst, forming a hyperbranched polyurethane having terminal hydroxyl groups.

Alternatively the precursor compound can contain two or more carboxylic groups (B') and a single hydroxyl group, for example 5-hydroxyisophthalic acid, or two or more primary amine groups (B') and a single primary or secondary alcohol group, for example N,N'-bis(3-aminopropyl)ethanolamine. Such a precursor compound can be reacted with carbonyl diimidazole to produce a compound containing a single hydroxyl group and two or more imidazolide groups. In the case of the diamine, a substantially stoichiometric amount of carbonyl diimidazole (2 moles per mole diamine) must be used. This compound can be polymerised by heating or addition of basic catalyst to form a hyperbranched polymer having terminal imidazolide groups.

It is generally preferred that compounds having functional groups on adjacent carbon atoms, such as glycerol or 2-amino-1,3-propanediol or diethylene triamine are not reacted with carbonyl diimidazole in the process of the invention, since such compounds tend to undergo a cyclisation reaction forming a cyclic carbonate, urethane or urea which is not useful in preparing hyperbranched polymers.

Hyperbranched polyureas can be formed by the reaction of a diprimary secondary triamine as precursor compound in which

the primary amine groups act as reactive groups B', for example dipropylene triamine, bis(hexamethylene) triamine or N-(2-aminoethyl)-propane-1,3-diamine, with carbonyl diimidazole at low temperature, preferably 0°C or below followed by heating to ambient temperature (e.g. 20 or 25°C) or above to polymerise the resulting AB₂ monomer. Secondary amine groups react with carbonyl diimidazole at room temperature or above but the imidazolidine formed is rather stable and does not readily react with any alcohol or amine groups. Secondary amine groups react readily with imidazolidine groups formed from primary amines, aromatic acids or primary alcohols. Primary amine groups react more rapidly with carbonyl diimidazole than do secondary amine groups. Thus if dipropylene triamine is reacted with carbonyl diimidazole at 0°C the preponderant product is



When this is polymerised, the hyperbranched polyurea product has a plurality of terminal imidazolidine groups. Alternatively a primary dissecondary amine can be reacted with carbonyl diimidazole to produce a compound containing one imidazolidine group and two secondary amine groups and this can be polymerised at room temperature or above to produce a hyperbranched polyurea.

Imidazolidine groups are generally reactive with amine groups and with most primary or secondary hydroxyl groups; a hyperbranched polymer having terminal imidazolidine groups can thus be used as a crosslinking agent in coating or sealant compositions. Alternatively, such a hyperbranched polymer can

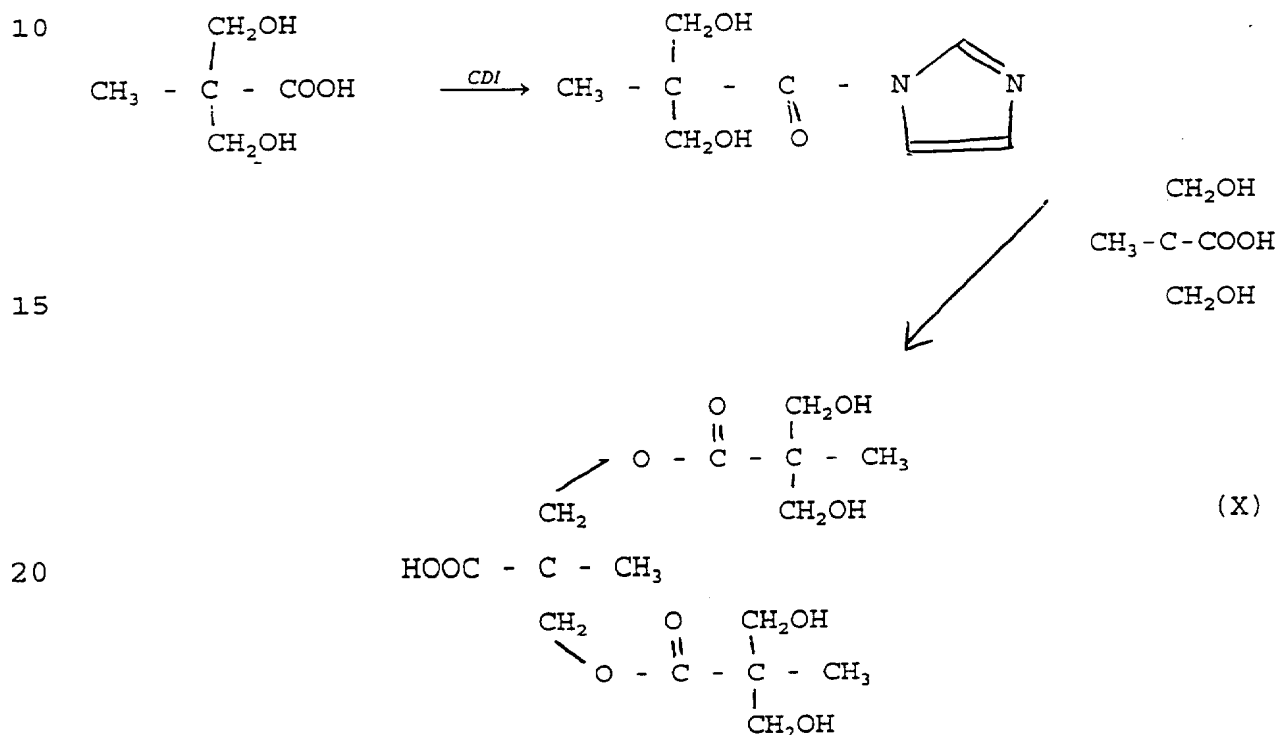
be reacted with a monofunctional amine or primary or secondary alcohol to form a non-functional hyperbranched polymer, or can be reacted with an amine or primary or secondary alcohol containing a functional group (C) not
5 reactive with the imidazolidine group, for example a carboxylic acid group to produce a hyperbranched polymer having functionality (C). Mixtures of reagents, for example a mixture of a monoamine and an aminoacid, can be used to form a hyperbranched polymer having a controlled number of
10 functional groups. Alternatively the hyperbranched polymer can be reacted with water to hydrolyse the imidazolidine group. For example the terminal imidazolidine groups of the hyperbranched polyurea described above can be hydrolysed to form terminal amine groups. Terminal imidazolidine groups
15 derived from a carboxylic acid hydrolyse very readily to form terminal carboxylic acid groups.

Any of the above processes can be modified to increase or decrease the degree of branching of the hyperbranched
20 polymer. The degree of branching can be decreased by the incorporation of an AB monomer, which can only form linear units, with the AB_2 monomer. For example a mixture of a dihydroxycarboxylic acid and a monohydroxycarboxylic acid such as lactic acid, gamma-hydroxybutyric acid or 2,2-
25 dimethyl-3-hydroxypropionic acid can be reacted with carbonyl diimidazole to produce a mixture of imidazolidines which act as AB_2 and AB monomers and can be polymerised by heating or by strong base catalyst to form a branched polyester containing an increased proportion of linear units.

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The degree of branching can be increased by the use of an AB_4 compound having a dendritic structure as all or part of

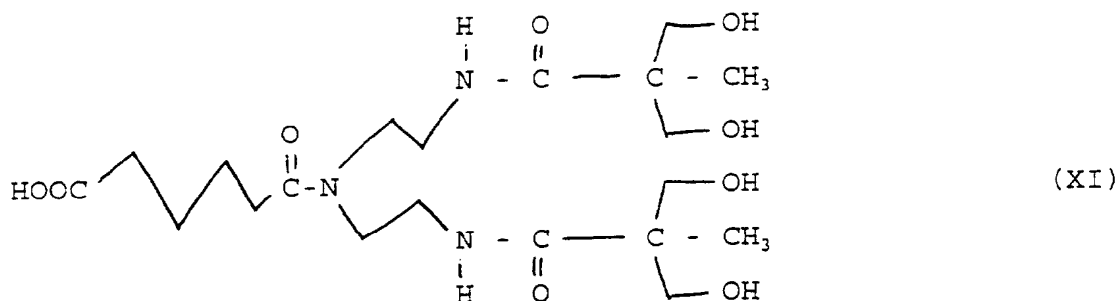
the monomer forming the hyperbranched polymer. For example a dihydroxycarboxylic acid such as bis(hydroxymethyl)propionic acid can be reacted with carbonyl diimidazole as described above and the resulting imidazolide can be reacted with
 5 further dihydroxycarboxylic acid by heating or in the presence of strong base catalyst to form a dendritic compound having one carboxylic acid group and four hydroxyl groups as shown below.



25 This can be reacted with carbonyl diimidazole to form an AB_4 monomer which can be polymerised to a hyperbranched polymer by heating or by a strong base catalyst.

30 Alternatively the imidazolide of a dihydroxycarboxylic acid can be reacted with a diaminocarboxylic acid such as an N,N-bis(2-aminoethyl) monoamide of a dicarboxylic acid to

prepare a dendritic compound containing one carboxylic acid group and four hydroxyl groups.



10 This can be reacted with carbonyl diimidazole to form an AB₄ monomer and polymerised by heating or by strong base catalyst to form a hyperbranched polymer containing both amide and ester linkages.

15 An alternative method according to the invention for the preparation of hyperbranched copolymers is by the copolymerisation of two or more different imidazolid compounds. Hyperbranched copolymers containing different
20 linkages can be prepared by copolymerising imidazolides in which the groups of formula (I) are different. For example the imidazolid of a dihydroxycarboxylic acid can be copolymerised with the imidazolid of a dihydroxyamine (in which the hydroxyl groups are primary or secondary alcohol
25 groups and the amine group is a primary or secondary amine group) such as N-(3-aminopropyl) diethanolamine to form a hyperbranched copolymer containing both ester and urethane links.

30 Thus, according to another aspect of the invention a hyperbranched polymer formed by the polymerisation of at least one compound containing a single group (A) of one

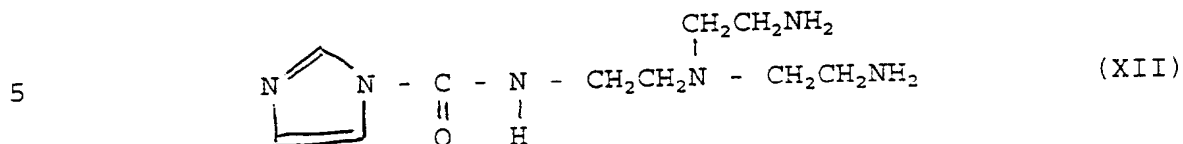
chemical type and at least two groups (B) of a different chemical type which is reacted with (A) is characterised in that the hyperbranched polymer is a copolymer containing two different chemical linkages, one of said linkages being
5 selected from urea, urethane and carbonate linkages and the other of said linkages being selected from urea, urethane, carbonate, ester and amide linkages.

Alternatively, hyperbranched copolymers containing both
10 aromatic and aliphatic groups can be produced by copolymerising two imidazolides, one of which is an aromatic compound such as the imidazolidine of 3,5-dihydroxybenzoic acid and the other of which is an aliphatic compound such as the imidazolidine of 2,2-bis(hydroxymethyl) propionic acid.

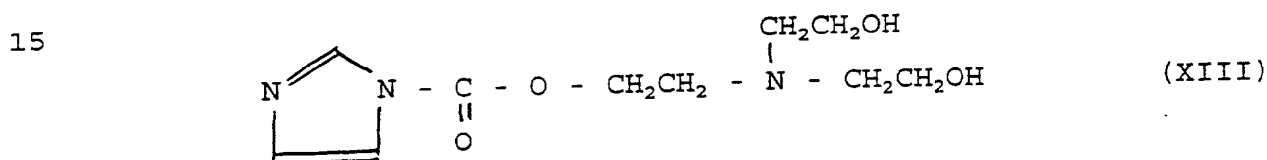
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A process according to another aspect of the invention for the preparation of a hyperbranched polymer is characterised in that a polyfunctional compound having at least three reactive functional groups (B) is reacted in
20 substantially equimolar quantities with a reagent which reacts rapidly with group (B) to form a group (A) which reacts more slowly with group (B). Examples of such reagents are carbonyl diimidazole and thiocarbonyl diimidazole, which react rapidly with primary amino groups or primary alcohol
25 groups to form imidazolidine groups which react less rapidly with the remaining primary amino or primary alcohol groups. The reaction with primary amine can be carried out at ambient temperature in the absence of catalyst. A strong base catalyst or elevated temperature, for example 50 to 120°C, is
30 needed with the alcohol. An example of a suitable tri(primary amine) is tris(2-aminoethyl)amine and an example of a suitable tri(primary alcohol) is triethanolamine. The

carbonyl diimidazole reacts rapidly with one primary amine group, predominantly forming the AB₂ monomer



before the subsequent slower reaction of the imidazolidine group with the primary amine groups to form urea linkages and eventually an amine-functional hyperbranched polyurea. We believe that hyperbranched polyureas have not previously been prepared. Similarly triethanolamine reacts rapidly to form predominantly



before the subsequent slower reaction to form carbonate linkages and eventually a hydroxy-functional hyperbranched polycarbonate.

The reagent which reacts rapidly with group (B) can alternatively be a compound containing two imidazolidine groups of formula (I), for example an imidazolidine of a dicarboxylic acid such as adipic or sebacic acid or an imidazolidine of a di(secondary or tertiary alcohol) such as hexane-2,5-diol or 2,5-dimethylhexane-2,5-diol or an imidazolidine of a di(primary amine) such as hexane-1,6-diamine. The imidazolidine of a dicarboxylic acid can be reacted with a primary triamine such as tris(2-aminoethyl)amine to produce a hyperbranched polyamide or with a triol such as triethanolamine to produce

a hyperbranched polyester. The imidazolidine of a diol can be reacted with a triol such as triethanolamine to produce a hyperbranched polycarbonate or with a primary triamine such as tris(2-aminoethyl) amine to produce a hyperbranched polyurethane. The imidazolidine of a diamine can be reacted with a primary triamine to produce a hyperbranched polyurea or with a triol to produce a hyperbranched polyurethane.

Alternatively, a compound containing three imidazolidine groups derived from a tri-carboxylic acid or a triol such as tris(2-hydroxypropyl)amine or a triamine such as tris(2-aminoethyl)amine can act as the polyfunctional compound having at least three functional groups (B), with for example a primary diamine acting as the reagent which reacts rapidly with group (B). The imidazolidine of a tricarboxylic acid can be reacted with a primary diamine such as ethylene diamine to produce a hyperbranched polyamide or with a diol such as pentane-1,5-diol to produce a hyperbranched polyester. The imidazolidine of a triol can be reacted with a primary diamine to produce a hyperbranched polyurethane or with a diol to produce a hyperbranched polycarbonate. The imidazolidine of a triamine can be reacted with a diamine to produce a hyperbranched polyurea or with a diol to produce a hyperbranched polyurethane.

25

Many of the hyperbranched polymers of the invention, have reactive functional groups at the surface and are thereby suitable for use as ingredients of high solids coatings and sealants; they can be cured through their functional groups to form solid coating films. They can also be used as reactive plasticisers in thermoplastic compositions. The hyperbranched polymers can alternatively be

used as rheology modifiers in coating and sealant compositions, causing a greater reduction of viscosity than a similar amount of volatile solvent.

5 Hyperbranched polymers having reactive functional groups at the surface can be used to bind biological reagents such as enzymes or antigens, as described for example in US-A-5229490, providing a high concentration of the biological reagent in a low molecular volume. Alternatively, new
10 colourants can be formed by attaching chromophores at the surface of the hyperbranched polymer.

In some uses it may be preferred to remove or reduce the number of surface functional groups. Hydroxyl groups can for
15 example be esterified. A hydroxy-functional hyperbranched polyurethane which is water-soluble is rendered water-insoluble if most of its hydroxyl groups are esterified to benzoate groups. Similarly amine functional groups can be converted to amide groups to reduce water solubility. The
20 surface functional groups can if desired be reacted with a compound containing a reactive functional group and one or more non-reactive groups which affect the properties of the polymer, for example fluoro or silicone groups to give low surface energy.

25

It will be seen from Figure 1 that the hyperbranched polymer contains one group A. It is assumed that this has become unreactive with groups B due to steric effect. This group A can be reacted with a compound having two or more
30 groups more reactive than group B to couple two or more hyperbranched polymer molecules. For example a hyperbranched polyester containing an imidazolidine group derived from a

dihydroxycarboxylic acid can be coupled by a di(primary amine).

The invention is illustrated by the following Examples:-

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Example 1

A solution of N-(3-aminopropyl)-diethanolamine (3.00g, 18.5 mmol) in tetrahydrofuran (THF) (30 ml) was added dropwise to a solution of carbonyl diimidazole (3.00g, 18.5 mmol) in THF (45 ml) and stirred at room temperature for 20 hours to form an imidazolidine.

Potassium hydroxide (0.1g, 1.8 mmol) was added to the reaction mixture and the solvent removed in vacuo. The residue was then heated at 120°C for 3 hours. THF (60 ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give a yellow gum. This was a hyperbranched urethane polymer of maximum molecular weight 6000 and number average molecular weight M_n 1075 as measured by MALDI (matrix assisted laser desorption ionisation mass spectrometry). The degree of branching was estimated at 0.6 by ^{15}N NMR.

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Example 2

A solution of bishydroxymethylpropionic acid (2.00 g, 15 mmol) and carbonyl diimidazole (2.40g, 15 mmol) in THF (60 ml) were stirred at room temperature for 2 hours.

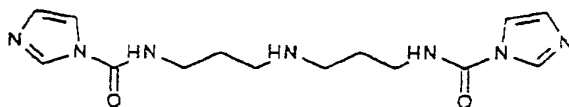
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Potassium hydroxide (0.2g, 3.6 mmol) was added to the reaction mixture and the solvent removed in vacuo. The

residue was then heated at 90°C for 3 hours. THF (60 ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give a colourless gum. This was a hyperbranched polyester of Mw 2426 and Mn 2421 as measured by MALDI. The degree of branching was measured as 0.49 by quantitative carbon-13 NMR; the chemical shift of the quaternary carbon atom varies according to whether it is surrounded by 3 ester units (dendritic unit), 2 ester units (linear unit) or one ester unit (terminal unit).

Example 3

A solution of dipropylene triamine (2.00g, 15mmol) in THF (10ml) was added to a solution of carbonyl diimidazole (4.95g, 30mmol) in THF (70ml) at 0°C and stirred at 0°C for 2 hours to form an AB₂ monomer of the formula:



(XIV)

Without isolation, the product was then reacted at room temperature for 20 hours. The reaction mixture was concentrated in vacuo to give a hyperbranched polyurea as a white sticky solid. Molecular weight was measured by MALDI and gave maximum molecular weights up to 3500.

Example 4

Carbonyl diimidazole (2.00g, 12mmol) was added to a

solution of trisaminoethylamine (1.80g, 12mmol) in THF (100ml) at 0°C and stirred for 4 hours at 0°C and then at room temperature for 18 hours. The THF was decanted, the residue dissolved in methanol and then concentrated in vacuo to give a hyperbranched polyurea as a yellow liquid. Molecular weight was measured by MALDI and gave maximums up to 3000.

10

Example 5

Carbonyl diimidazole (3.63g, 22mmol), trimethylolpropane (3.00g, 22mmol) and potassium hydroxide (0.2g, 3.5mmol) in THF (50ml) were heated at 60°C for 3 hours. The solvent was removed and the residue heated at 60°C for a further 3 hours to give a hyperbranched polycarbonate as a colourless gum. Molecular weight was measured by MALDI and gave maximums up to 5000.

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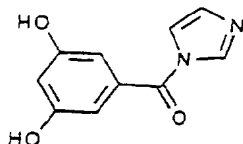
Example 6

Carbonyl diimidazole (3.00g, 19mmol) was added to sebacic acid (1.87g, 9.3mmol) in methanol (50ml) and stirred at room temperature for 2 hours to form the bis(imidazolide) of sebacic acid. Trisaminoethylamine (1.35g, 9.3mmol) was added to the solution and the reaction stirred at room temperature for 96 hours then concentrated in vacuo to give a hyperbranched polyamide as a yellow liquid.

30

Example 7

A solution of 3,5-dihydroxybenzoic acid (2.00g, 13mmol) and carbonyl diimidazole (2.1g, 13mmol) in THF (60ml) was stirred at room temperature for 2 hours to form an imidazolide of the formula:

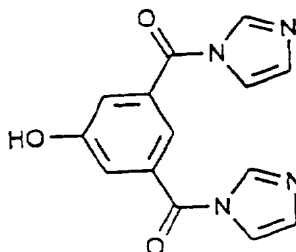


(XV)

Potassium hydroxide (0.2g, 3.6mmol) was added to the solution and the reaction mixture stirred at room temperature for 24 hours then concentrated in vacuo. Water was added to the residue and the pale brown precipitate filtered and dried in vacuo to give a hydroxy-terminated hyperbranched polyester as a brown solid. Molecular weight was measured by MALDI and gave maximums up to 3500.

Example 8

A solution of 5-hydroxyisophthalic acid (1.69g, 9.3mmol) and carbonyl diimidazole (3.00g, 19mmol) in THF (60ml) was stirred at room temperature for 2 hours to form a bis(imidazolide) of the formula:



(XVI)

The solvent was removed and the residue heated at 90°C for 3 hours and cooled. THF was added to the residue, the white precipitate was removed by filtration and dried in vacuo to give a hyperbranched polyester as a white solid. Molecular weight was measured by MALDI and gave maximums up to 6000. The hyperbranched polyester had terminal acid functionality as a result of hydrolysis of imidazolide groups by ambient moisture during work-up.

10

Example 9 -Synthesis of a Hyperbranched
Polyester/Polyurethane Copolymer

Step 1: A solution of 3-aminopropyldiethanolamine (3.00g, 19mmol) in THF (30ml) was added to a solution of carbonyl diimidazole (3.00g, 19mmol) in THF (45ml) and stirred at room temperature for 20 hours to form imidazolide (VIII).

Step 2: A solution of bishydroxymethylpropionic acid (2.48g, 19mmol) and carbonyl diimidazole (3.00g, 19mmol) in THF (60ml) was stirred at room temperature for 2 hours to form imidazolide (VII).

Step 3: The reaction mixtures produced in steps 1 and 2 were combined and concentrated in vacuo. The residue was heated at 90°C for 3 hours and cooled. THF (100ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give the copolymer as an orange gum.

Example 10 - Synthesis of a Hyperbranched Aliphatic Polyester/Aromatic Polyester Copolymer

Step 1: A solution of 3,5-dihydroxybenzoic acid (1.90g, 12mmol) and carbonyl diimidazole (2.00g, 12mmol) in THF (60ml) was stirred at room temperature for 2 hours to form imidazolide (XV).

Step 2: A solution of bishydroxymethylpropionic acid (1.65g, 12mmol) and carbonyl diimidazole (2.00g, 12mmol) in THF (60ml) was stirred at room temperature for 2 hours to form (VII).

Step 3: The reaction mixtures produced in steps 1 and 2 were combined and concentrated in vacuo. The residue was heated at 90°C for 3 hours and cooled. THF (100ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give the copolymer as a pale brown solid.

Example 11 - Modification of the Surface Functionality of a Hyperbranched Polyurethane

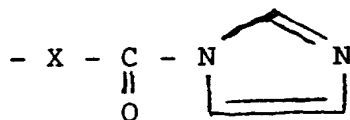
A solution of benzoic acid (0.57g, 4.7mmol) and carbonyl diimidazole (0.76g, 4.7mmol) in THF (30ml) were stirred at room temperature for 2 hours to form the imidazolide. The imidazolide so prepared was added to the hydroxy-terminated hyperbranched polyurethane produced in Example 2 (0.76g) and potassium hydroxide (0.1g, 1.7mmol) and the reaction mixture stirred at 60°C for 5 hours. The reaction mixture was

concentrated in vacuo to give the hyperbranched polyurethane terminated with benzonate ester groups. NMR analysis revealed the presence of the benzoate ester groups and the absence of any hydroxyl groups indicating that complete reaction of all
5 of the original hydroxy groups had occurred.

CLAIMS

1. A process for the preparation of a hyperbranched polymer, characterised in that a polyfunctional compound having three reactive functional groups (B) is reacted in substantially equimolar quantities with a reagent which reacts rapidly with group (B) to form a group (A) which reacts more slowly with group (B).
2. A process according to claim 1, characterised in that the reagent is carbonyl diimidazole and the groups (B) are primary amine or primary alcohol groups.
3. A process according to claim 1, characterised in that the reagent is an imidazolid containing two groups of the formula:-

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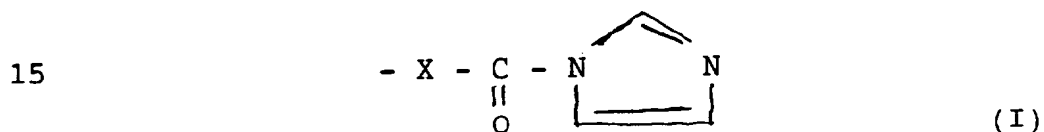
(I)

where Q represents O or S and X represents -O-, -S-, -NH- or a direct bond, the group being linked to the remainder of the compound through a carbon atom, and the polyfunctional compound is a tris(primary amine) or a tris (primary alcohol).

4. A process according to claim 1, characterised in that the said polyfunctional compound is an imidazolidine containing three groups of the formula (I) as defined in claim 4 and the reagent is a compound containing two primary amine or primary alcohol groups.

5. A hyperbranched polymer characterised in that all or most of the chemical linkages in the polymer are urea linkages.

6. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that the single group (A) is a group of the formula:

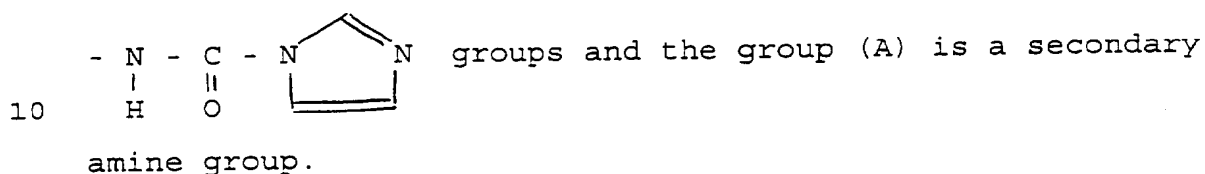


7. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that either the group (A) or the group (B) is a group of the formula:



where Q represents O or S and X' represents -NH- or a direct bond, the group being linked to the remainder of the compound through a carbon atom.

- 5 8. A process according to claim 7 for the preparation of a hyperbranched polyurea, characterised in that the groups (B) are



9. A process according to claim 7 for the preparation of a hyperbranched polyester, characterised in that the group (II) is a $\begin{array}{c} \text{C} - \text{N} \\ || \quad \diagup \quad \diagdown \\ \text{O} \quad \text{C} = \text{C} \end{array}$ group and the other group (A) or (B) is a hydroxyl group.

10. A process according to claim 7 for the preparation of a hyperbranched polyurethane, characterised in that the group (II) is a $\begin{array}{c} \text{N} - \text{C} - \text{N} \\ | \quad || \quad \diagup \quad \diagdown \\ \text{H} \quad \text{O} \quad \text{C} = \text{C} \end{array}$ group and the other group (A) or (B) is a primary or secondary alcohol group.

- 25 11. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that a precursor compound, containing either
30 a single group (A') of one chemical type reactive with carbonyl diimidazole and at least two groups (B) of a different chemical type from A' which is less reactive than

A' with carbonyl diimidazole or at least two groups (B') of one chemical type reactive with carbonyl diimidazole and a single group (A) of a different chemical type from B' which is less reactive than B' with carbonyl diimidazole, is
5 reacted with carbonyl diimidazole under conditions such that only the group A' or the groups B' react with the carbonyl diimidazole to form imidazolide groups and the resulting compound containing imidazolide groups is polymerised under more vigorous reaction conditions to form the hyperbranched
10 polymer.

12. A process according to claim 11 for the preparation of a hyperbranched polyester, characterised in that the group A' or groups B' of the precursor compound are carboxylic acid
15 groups and the groups B or A respectively of the precursor compound are hydroxyl groups, and the more vigorous reaction conditions comprise heating or catalysis by a basic catalyst.

13. A process according to claim 11 for the preparation of a
20 hyperbranched polyurethane, characterised in that the group A' or groups B' of the precursor compound are primary amine groups and the groups B or A respectively of the precursor compound are primary or secondary alcohol groups, and the more vigorous reaction conditions comprise heating or
25 catalysis by a basic catalyst.

14. A process according to claim 11 for the preparation of a hyperbranched polyurea, characterised in that the precursor compound is a diprimary secondary amine and is reacted with
30 carbonyl diimidazole at 0°C or below, and the more vigorous reaction conditions comprise a higher temperature which is ambient temperature or above.

15. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that either the group (A) or the group (B) is a group of formula (I) as defined in claim 6 and in that a hyperbranched copolymer is formed by polymerising together at least two such compounds.

10

16. A process according to claim 15, characterised in that the groups of formula (I) in one of the said two compounds are different from the groups of formula (I) in the other compound.

15

17. A process according to claim 15, characterised in that one of the said two compounds is an aromatic compound and the other is an aliphatic compound.

18. A hyperbranched polymer formed by the polymerisation of at least one compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reacted with (A), characterised in that the hyperbranched polymer is a copolymer containing two different chemical linkages, one of said linkages being selected from urea, urethane and carbonate linkages and the other of said linkages being selected from urea, urethane, carbonate, ester and amine linkages.

30



Application No: GB 9709045.0
Claims searched: 1-4

Examiner: Alan Kerry
Date of search: 28 July 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3R RSM, RSP

Int Cl (Ed.6): C08G 63/06, 64/38, 69/24, 71/02, 71/04

Other: Online databases: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	Macromolecules, Vol. 30, No. 7, pp. 1890-1896 (1997)	1
X	Macromolecules, Vol. 25, No. 21, pp. 5561-5573 (1992)	1

X Document indicating lack of novelty or inventive step
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